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# "LIGHT SCATTERING FROM MACROMOLECULAR SYSTEMS - MOLECULAR CRYSTALS AND POLYMERS"



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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

During the funding period, significant theoretical and experimental advances have been made in this research. Experimentally, a novel and unique apparatus has been constructed to measure light scattering from crystal, liquid crystal, and polymer samples. This system has a frequency range for low frequency motion in the samples between 30 GHz and 100 MHz and $10^6$ Hz and 1 Hz. Both Brillouin and correlation spectra have been observed and studied from triazine, trioxane, chloranil, benzil, a lyotropic

20. liquid crystal and various polymer samples. Theoretically, a number of calculations and descriptions of phase transition and critical phenomena of various types have been generated. It has been possible to model all the thermodynamic behavior that has been charaterized to date.

## WORK STATUS OF THE RESEARCH EFFORT

Research Objectives: of this grant are to

(1) characterize phase transitions theoretically and experimentally in molecular crystal systems,

(2) use the above understanding gained by light scattering studies and theoretical interpretation to apply to the more complex system of lyotropic liquid crystals, and

(3) knowledge gained on the model systems of increasing complexity is then applied to polymer liquid crystals and solid polymers as observed by laser light scattering techniques.

Objective one has been definitely achieved as can be seen from the number of papers written in the last few years. Systems to have been experimentally and theoretically discussed are: trioxane, triazine, benzil, and chloranil. Others are still be investigated: biphenyl, urea, thiourea, and hexamethyl benzene. We have developed a nean field thermodynamic theory to trial all these results which are not based on critical fluctuations. Equations of motion techniques have been used to present discussions of critical behavior observed in triazine, chloranil, and benzil.

Benzil is a particularly interesting system in terms of more complex polymeric systems because it evidences defect dominated light scattering, correlation behavior, and critical phenomena. It also responds to external stress with a critical correlation function. All of these phenomena have been modeled and explained using the theory of inelastic solids. This is an important finding and treatment because of its application to polymeric systems.

Studies of lyotropic liquid crystals (sodium decyl sulfate, sodium sulfate, decanol, water) have been progressed to the point at which we will be reporting this data shortly. The major findings are: a number of phase transitions occur between 20 and 60°C; these transitions evidence strong critical behavior and

long correlation times for fluctuations; and liquid crystals can be studied by light scattering in a unique and meaningful manner. Based on these data we believe that various transitions take place in these lyotropic liquid crystals involving micelle-micelle interactions, hydrocarbon chain reorganizations, and polar head group/counterion/$H_2O$ reorganizations at the micelle surface.

Finally, some polymer studies were started which will be continued into the coming contract period. Spectra of solid powders, ribbons, and liquid crystals of PBT and solid PBO were obtained. At present we need more general background development on model systems in order to interpret these polymer light scattering data. The details of these studies are presented below.

These studies initiated with exploratory work on transition metal hexafluorides in 1975-1977. Much of these investigations were carried out under AFOSR support. The work involved a detailed elucidation of the inter- and intramolecular modes of transition metal hexafluorides and can be divided into three separate parts summarized below.

I. Orthorhombic $MoF_6$, $WF_6$, and $UF_6$ Neat Crystals

Raman spectra of neat crystals of $MoF_6$, $WF_6$, and $UF_6$ have been obtained and discussed in terms of the internal and external modes of the molecules. The spectra of the fundamental regions are consistent with factor group predictions based on the published crystal structures. Molecular and crystal Fermi resonances are important in understanding differences between the various crystal spectra and for explaining intensity distributions. The excitonic structures are remarkably alike when energy scales are normalized for each fundamental region. The similarity is a crystal phenomena and the energy scaling is attributed to differences in molecular properties (e.g., polarizability and electric dipole derivatives). The external modes have been fit to a model treating the optical phonons as crystal independent pure translational and librational normal modes.

## II. Two-Particle and Mixed Crystal Spectra as Techniques for Determination of Densities of States

The major conclusions of this phase of study are:

1. The major Raman intensity mechanism for the transitions to higher vibrational levels in these crystals is the second order transition operator rather than the first order transition operator acting in conjunction with anharmonic mixing of levels (at least for the $\nu_1$ modes).

2. Many of the combination and overtone bands in these crystals display two particle character.

3. Accurate information concerning the density of states of a fundamental vibrational exciton band can be obtained from the two-particle band corresponding to combination with the $\nu_1$ mode.

4. The two-particle determined density of states has allowed an evaluation of the appropriate mixed crystal concentration region in which k selection rules are significantly destroyed but in which band structure is not greatly altered.

## III. Exciton Band Structures of $MoF_6$, $WF_6$, and $UF_6$

The vibrational exciton bands of $MF_6$ (M - Mo, W, U) have been investigated through the Raman spectra of neat and mixed crystals. Site energies (gas-to-crystal shifts), $\underline{k} = 0$ structure, $\underline{k} \neq 0$ dispersions, and the densities of states have been examined using fundamental band neat and mixed crystal spectra, two-particle ($\nu_1 + \nu_i$) neat crystal spectra, and $\nu_2$ and $\nu_5$ quadrupole-quadrupole calculations as sources of information.

The individual neat crystal bands have been understood in terms of electrostatic multipole models with the scaling between crystals or bands of the same crystal being reasonably consistent with molecular parameters (dipole derivatives, particle charges, bond distance, amplitudes of vibration, electronic polarizability).

In discussing site energies (or band centers) and intensities of Raman

spectra, crystal induced Fermi resonances were found to be important. The $\nu_6$ mode evidenced the effects of additional potential energy terms on a low energy vibration.

In discussing dilute mixed crystals it becomes apparent the pseudoresonances were important. This appears somewhat at odds with the fact that the band structures are relatively independent of the compound and its exact distribution of vibrational energy levels and resonance mechanisms. It may be that the interaction between bands is partially projected onto a band center shift term. Such overall band shifts can be incorporated quite nicely into a general crystal induced Fermi interaction. The remaining differential shift terms, which change relative $\underline{k} = 0$ positions, may be small. These interactions which appear most prominently in the bending region, may be associated with the inability to obtain an accurate fit of the calculated $\nu_5$ $\underline{k} = 0$ structure with that observed for $UF_6$ ( most clearly resolved). A good fit to the $\nu_2$ bands of $MoF_6$ and $UF_6$ is obtained with the same quadrupolar calculation.

The concept of the ideal mixed crystal has been shown not to be rigorously correct for the mixed crystal vibrational properties of $MoF_6$ or $WF_6$ with $UF_6$.

Our first real phase transition studies came about from $SiF_4$ and $GeF_4$ work arising from our interests in $MF_6$ systems. The Raman scattering spectra of large single crystal of $SiF_4$ and $GeF_4$ at 77 K are reported. These data have been reinterpreted based on the absence of any observable changes in the spectra for scattering angles between 0° and 90°. The previous assignment of the dipole allowed $\nu_3$ and $\nu_4$ modes based on a TO/LO splitting model is thereby shown to be incorrect. In the absence of an apparently correct crystal structure, an exact interpretation of the data in terms of a factor group-exciton analysis is not possible; nonetheless, all observations appear to be consistent with a centrosymmetric space group having a multimolecular primitive unit cell. Mixed $SiF_4$/$GeF_4$ crystal spectra have also been obtained which demonstrate that $GeF_4$ does not substitute into the $SiF_4$ lattice but the $SiF_4$ does enter the $GeF_4$ crystal substitutionally

The Raman scattering spectrum of $GeF_4$ is somewhat simpler than that of $SiF_4$. Splitting of the low energy components of $\nu_3$ and $\nu_4$ has not been observed. Either the crystal structure of $GeF_4$ is closer to an ideal high symmetry space group than is that of $SiF_4$ or spatial dispersion in $GeF_4$ is smaller than that of $SiF_4$.

Failure of $GeF_4$ to occupy simple unique (substitutional) sites in $SiF_4$ is observed, as is the apparent exclusion of $GeF_4$ at moderate concentrations, even though the neat crystals have nearly equal molecular packing densities.

The polariton model for the $\nu_3$ and $\nu_4$ vibrations is not successful in explaining the observed 0° and 90° Raman spectra of $SiF_4$ or $GeF_4$. The main unique feature of this model crystal orientation and/or scattering angle dependent spectra; neither of these effects has been observed. We would suggest that the observed splittings previously assigned as transverse and longitudinal components are gerade Davydov components of dipolar exciton bands. The polariton dispersion curves in this case would be drastically altered; the electromagnetic field vibrations must couple with ungerade unit cell mechanical vibrations. This would remove the expectations for angle and crystal orientation dependent Raman spectra.

A detailed study of the structure and interactions in these molecular crystals seems warranted. There are several ambiguities in the vibrational spectra which could thereby be resolved. Moreover, careful polarization studies on oriented single crystals would then be worthwhile.

The studies of $SiF_4$, $GeF_4$, $MoF_6$, $UF_6$, and $WF_6$ lead us to investigate the general phenomena of phase transitions and polaritons in molecular crystals. This work has been quite successful and has opened up the general area of polymer and liquid crystal work to us.

We report the first observation of phonon-polariton modes in a molecular solid - sym-triazine. Lattice vibrations which carry an electric dipole moment have radically different properties from non-polar vibrations. The dipole

moment couples the lattice vibration to the internal radiation field present in the crystal to form mixed excitation modes, part phonon, part photon, which have a characteristic dispersion (k vs. ω or momentum vs. energy) relation and are known as polaritons. Study of polariton dispersion relations is most easily and rigorously performed by near forward (0° - 10°) direction angle dependent Raman scattering, angle dependent infrared reflection and absorption measurements being rather insensitive. Experimental observation of phonon-polaritons is thereby typically confined to non-centrosymmetric structures.

Study of polaritons through their dispersion relations leads to a fuller understanding of radiation-matter interactions and the range and anisotropy of intermolecular forces. Sym-triazine is an excellent molecule/molecular solid for such a study considering its simplicity, high molecular and crystal symmetry, ease of crystal growth from melt or vapor, and importance as a prototype for other aromatic azine systems. Moreover, triazine forms a uniaxial room temperature crystal, one of the few molecular systems to do so, making directional, polarization, and crystal tensor properties relatively easy to treat.

Sym-triazine supplied by Aldrich Chemical Co. was fused with potassium, distilled through molecular sieve, and single crystals were grown by sublimation. To measure accurate angle-dependent Raman scattering, an experimental set-up was developed which is similar to that reported by Claus et al. To calibrate this new apparatus the well-known polaritons in α-quartz were studied. Small angle Raman spectra were recorded in the intra- and intermolecular region by varying the scattering angle (θ) inside the crystal from 0.3° to 6.5°. Polariton shifts were observed for transverse optic (TO) phonons at 1072, 797, nad 450cm$^{-1}$ along the tensor component $\alpha_{zx}$. A dispersion curve (ω vs. k (θ)) was plotted for the 450cm$^{-1}$ mode and found to be in excellent agreement with previous experimental and theoretical results.

In order to observe polariton effects in a molecular solid similar experiments

were performed on oriented single crystals of sym-triazine at room temperature. Scattering angle was varied between 0° and 5.1° in the near forward direction. The only appreciable polariton dispersion observed was for a phonon at about 70 $cm^{-1}$ (90° scattering) assigned as a rotatory lattice mode of E symmetry (see below). Figure 1 shows the polariton shift for this phonon as a function of scattering angle. The dispersion curve for this mode is presented in Figure 2, which collects data obtained for two different crystals taken months apart prepared and treated separately. Small polariton shifts can be expected for molecular solids.

In order to determine whether or not any of this ~3 $cm^{-1}$ dispersion could be associated with crystal anisotropy effects, a single crystal of sym-triazine was accurately oriented in the laser beam by conoscopic techniques. Spectra were obtained as a function of angle on different crystal faces, at different polarizations, and at different orientations of $\underline{k}$ with respect to the optic axis. In all cases polariton shifts remain only a function of the scattering angle. Thus, we are confident that the major fraction of the observed dispersion is due to polariton (phonon-photon) coupling and not crystal anisotropy.

These results confirm the fact that in molecular solids in general, and triazine in particular, dipolar and long-range forces are small and indeed that the coupling between radiation and mechanical modes in molecular solids is much smaller than it is in ionic solids. In addition, these observations allow certain deductions concerning the room temperature crystal structure of sym-triazine to be made. The crystal structure of sym-triazine at room temperature has been assigned as $D_{3d}^6$ ($R\bar{3}c$), with two molecules per primitive unit cell at sites of $D_3$ symmetry. Aside from any difficulty there might be with placing triazine at a $D_3$ site, observation of polariton dispersion through Raman scattering precludes this centrocentric structure from being correct. This conclusion is based on the fact that only u-vibrations carry dipole moments and they would be Raman inactive in a centrosymmetry structure. The crystal is most likely of R3c ($C_{3v}^6$) symmetry

with molecules at $C_3$ sites, the non-centrosymmetric image of $R\bar{3}c$. The original structural data were never refined in the non-centrosymmetric group. The molecule in the crystal is thereby non-planar ($C_3$) and it is probable that this small non-planarity is disordered in the crystal; the averaged structure may well retain a center of inversion.

We are presently exploring polariton behavior in this and other molecular solids (e.g., trioxane) both theoretically and experimentally. Data are being collected as a function of temperature and in various crystal phases in order to understand more fully the extent and nature of polariton couplings in molecular crystals. It is, moreover, of interest to determine if such modes have any special behavior with regard to solid-solid phase transformations. Calculations based on intermolecular potentials, indices of refraction, and static dielectric constants are being pursued.

These early studies of phase transitions in molecular solids wetted our interest and progressed to much more detailed studies of trioxane, triazine, benzil, chloranil, and others. These investigations are reviewed below in chronological order.

Polarized Raman spectra of sym-trioxane single crystals have been recorded in the intra- and intermolecular regions. Three phonons were observed at room temperature at 59.6, 64.3, and 84.8cm$^{-1}$ belonging to E symmetry. Temperature dependent Raman spectra were also recorded which showed the following important features: (a) polarization data could not be obtained below ca. 65 K: (b) the phonon at 85cm$^{-1}$ (300K) splits into two modes at 63K and the splitting grows continuously to 1.6K, the lowest temperature reached in this study: (c) the phonons at 60 and 65cm$^{-1}$ (300K) show a constant-slope linear increase in energy from 300 to 65K at which point the slope changes considerably: and (d) linewidths of these latter two modes evidence discontinuous changes at 63K. Temperature dependence of the observed ($T_x$, $T_y$) phonon splitting follows approximately an equation of the form $\eta(T)/\eta(1.6K) = |(T_c-T)/T_c|^{k}$. The phase transition is

discussed in terms of various mechanisms and models which could be applicable in the absence of distinct soft mode features.

Our most extensive work to date has been theoretical and experimental studies of sym-triazine. Triazine has served as a model system for molecular crystals as well as polymers and liquid crystals because, we believe, the motions and interactions observed for this system are quite general. Rotations, translations, and rotation-translation coupling control dynamics in all weakly bound molecular systems.

A Landau mean field description of the nearly second order phase transition in sym-triazine crystals at ~ 200K is presented. A model Hamiltonian is generated which consists of the appropriate symmetry elastic constant terms, molecular rotational energy, and rotation-translation coupling terms (to second order in both strains and rotations). Due to the symmetry of the crystal in the high ($R\bar{3}c$) and low C2/c) temperature phases, third order terms in the rotational order parameter are nonvanishing; the transition is thereby a first order one (although only weakly so). This Hamiltonian is then converted to a free energy by addition of an entropy term calculated for an orientation distribution (about the z axis) based on pocket state functions. The Landau mean field model is developed by choosing a set of order parameters $R_y$ (molecular rotation about the y axis) and strains $e_5$ and $(e_1-e_2)$. The free energy expression is used to calculate relations between order parameters by setting $\partial F/\partial R_y = \partial F/e_5 = \partial F/ e_7 = 0$. Coupling terms including bilinear products of $e_p$'s and $R_y$ are employed in this development. Renormalized temperature dependent elastic constants are derived. $e_5(T)$ is solved for and found to be in good agreement with observed temperature dependences. Librational frequencies are determined from $(\partial^2 H/\partial R_i R_j)e_p = I\omega_i^2 \delta ij$. It is found that in the low temperature phase $\Delta\omega = |\omega_y-\omega_x| \propto e_5$ in the lowest order. Observed power laws for frequencies, splittings and strains with respect to $\epsilon \equiv (T-T_c/T)$ are discussed in light of these new results. The role of third order terms in $(R_x,R_y)$ is considered and found to be an important factor in apparent

deviation from mean field exponents.

This study has presented a relatively complete theoretical description of the sym-triazine trigonal-monoclinic phase transition in the mean field Landau limit. The transition is seen to arise from a coupling between shear (transverse) acoustic modes associated with elastic constant $c^o_{44}(e_4e_5)$ and molecular rotations out of the basal plane $(R_x,R_y)$. The Hamiltonian of the crystal is found to consist of three contributions: orientational, elastic, and the rotation-translation coupling. This coupling leads to an indirect orientation-dependent interaction between triazine molecules. This indirect coupling is added to the direct orientation dependent triazine-triazine interactions which consist mainly of electronic overlap and octupole contributions. It is this indirect interaction which overcomes a very strong orienting crystal field and brings about the structural transformation.

Within the Landau mean field theory, expansion of the free energy of the crystal has been written in terms of the strains $(e_4,e_5,e_6,e_1-e_2)$ and the rotations $(R_x,R_y)$. In the neighborhood of the transition all expansion coefficients, except the one for the $(R_x^2 + R_y^2)$ orientational term, are assumed to be temperature independent. For this term the usual $a_0(T-T_0)$ dependence is used. This temperature dependence of the quadratic term in the free energy expansion can arise from either or both of the following contributions: an effective orientational field experienced by a single molecule in the environment of its neighbors, which is temperature dependent, and an entropy contribution due to a change in the orientational distribution function.

The specific heat anomaly associated with the structural transformation in triazine is similarly made up from the following contributions: an orientational ordering term, and a lattice dynamical term. The lattice dynamical specific heat contribution is a function of the Debye temperature of the crystal. One would expect an anomaly in the specific heat to be due to both rotational ordering (entropy terms) and the softening of the transverse acoustic phonon velocities

$\nu_{TA}$ in certain directions in the Brillouin zone.

If the lattice dynamical terms dominate the orientational entropy contributions, the transition might be classified "displacive" rather that "order disorder." This is probably the case for triazine since the extent of the disorder in the high temperature phase seems to be small. The details of the temperature dependence of the orientational distribution function remain to be worked out.

The structural transformation in triazine is found to be weakly first order. The elastic constants $c_{44}$, $\frac{1}{2}(c_{11}-c_{12})$, and $c_{14}$ all exhibit a strong temperature dependence near the transition, but do not actually vanish because of the first order character of the transition. The elastic constant $c_{44}$ shows the strongest temperature anomaly. A comparison of the predicted temperature dependence of the strain order parameter $e_5$ with experiment indicates an improvement over a simple $(T-T_c)^{\frac{1}{2}}$ mean field power law. This is mainly due to the cubic term in the free energy which produces a discontinuity of the order parameter at the transition.

Based on the coupled Hamiltonian, librational frequencies are calculated at constant values of the strains. These frequencies are different for $R_x$ and $R_y$ librations with a first order splitting proportional to the order parameter for the transition $e_5$. However, $e_5$ must be small for this approximate relationship to hold.

We have then elaborated on this theory to include dynamical behavior as observed in light scattering experiments. Such an approach allows us to explain many more experimental observations. A description of the phase transition in sym-triazine on an Onsager equations of motion approach is presented. Using a Hamiltonian which includes the full dynamics (kinetic and potential energies) of the coupled rotations and translations, Green's functions and correlation functions for librational and acoustic modes are obtained. The method employed here is similar to psuedo-spin phonon theories in which spin coordinates are higher order rotational variables such as $R_xR_y$ and $(R_x^2-R_y^2)$. Calculations for phonon groups in the small oscillator limit are presented and compared with neutron scattering data between 300K and 205K ($T_c \sim 198K$). Good agreement is obtained outside the immediate region of the phase transition (T > 205K).

These theoretical studies are demonstrated to be correct by our light scattering studies of triazine. Both correlation and Brillouin scattering experiments have been done. The experimental apparatus is unique for this total light scattering system and its description has been published in J. Chem. Phys. (to appear) by A. Yoshihara, C.L. Pan, E.R. Bernstein and J.C. Raich.

We have investigated the ferroelastic phase transition in sym-triazine around 197K by Brillouin scattering and correlation spectroscopy. Our observations are summarized as follows:

1. A soft mode whose squared frequency satisfies a mean field result given by

$$\omega_S^2 = (\omega_S^0)^2 \frac{T-180}{T+759}$$

was characterized. This $c_{44}$ instability is considered as the physical origin of the phase transition.

2. No well defined central peak could be observed in the Brillouin spectra, but a 50% increase of the Rayleigh intensity was observed near the transition temperature in the high temperature phase.

3. A second independent, temperature dependent TA-phonon was observed which also satisfies mean field behavior:

$$(\omega_S')^2 = (\omega_S'^0)^2 \frac{T-17}{T+759} .$$

This mode is interpreted as a result of a $c_{66}$ instability not directly "related to" or "driven by" the $c_{44}$ "main" instability.

4. The LA-phonon does not show any anomaly even near the transition temperature.

5. Correlations in the Rayleigh scattering were not observed at any temperature ($T \geq T_c$) between roughly $10^{-6}$ sec and 1 sec.

These results are interpreted by a Landau mean field theory and a dynamical theory. Both approaches give a consistent explanation for the static and dynamic Brillouin and neutron scattering data. Based on the dynamical theory, the phase transition in sym-triazine can be regarded as an example of the fast

relaxation case which is characterized by a soft mode phonon response without a central peak.

Finally, the possibility of critical fluctuations was examined using the Rayleigh intensity and correlation results. These data suggest that the only possibility for fluctuation effects near the transition temperature is for fluctuation frequencies smaller than 1 Hz or between 10 MHz and 1 GHz.

Using the experimental and theoretical techniques developed for triazine we have approached a more complicated system - benzil. The phase transition in crystalline benzil $[(C_6H_5CO)_2]$ at 84K is investigated through Brillouin scattering. The major experimental findings are: two transverse acoustic phonon modes exhibit softening near the phase transition; a longitudinal acoustic mode is temperature sensitive; and the ratio of the Rayleigh peak intensity to the soft mode intensity behaves anomalously. These results are discussed using a theory developed for an elastic phase transition in sym-triazine, $(C_3N_3H_3)$. It is found that bilinear coupling terms involving strains and the order parameter can explain transverse mode behavior but not that of the longitudinal acoustic mode.

The structural phase transition in benzil at 83.5K has been investigated using Brillouin scattering from phonons propagating along the a- and c-axes. Our observations are summarized as follows:

1. Two transverse modes propagating along the a- and c-axes behave as soft modes. The related elastic constants are $\frac{1}{2}[(c_{66}+c_{44}) - \sqrt{(c_{66}-c_{44})^2 + 4c_{14}^2}]$ and $c_{44}$, respectively.
2. A longitudinal phonon propagating along the a-axis is temperature sensitive near the transition point; a $\lambda$-type anomaly is observed for this mode.
3. A longitudinal phonon propagating along the c-axis shows no anomaly around the transition temperature as predicted by the triazine Landau theory.
4. The ratio of the soft mode intensity to Rayleigh peak intensity along the a-axis was examined. It was found that this ratio has a maximum at $T_c$+1K

which indicates a rapid increasing in the Rayleigh intensity in the high temperature phase.

5. Anisotropy of phonon frequencies in the a-c plane was determined at room temperature. These results are analyzed by a mean field Landau theory. Observed elastic constant temperature dependences could be fitted by a relation of the form,

$$c = c_0(T-T_2)/(T-T_1)$$

Along the a-axis in the high temperature phase $c_{0T} = 0.107 \times 10^{10} N/m^2$, $T_2 = 74.4K$ and $T_1 = T_0 = 37.2K$ and $c_{0L} = 1.58 \times 10^{10} N/m^2$, $T_2 = 73.4K$ and $T_1 = 72.6K$.

Bilinear coupling constants appearing in the theory could be estimated from the data. To discuss the $\lambda$-type anomaly in $c_{11}$, an electrostrictive type interaction was introduced. This term also contributes to the elastic softening in the high temperature phase. The effect of a Brillouin zone boundary instability on the elastic constants was examined and it was found to give contributions similar to those for the electrostrictive interactions from zone center order parameters. A quantitative decomposition of these two contributions must await a more complete and more accurate data set.

Anisotropy in phonon frequencies was calculated based on the triazine theory, and good agreement between theoretical and experimental results obtained.

Finally, a possibility of some (dipolar) relaxation process was explored to explain sound velocity dispersion, Rayleigh intensity and the dielectric anomaly in benzil. Rayleigh correlation measurements are now in progress to obtain more information on this relaxation phenomenon.

Upon more detailed investigations even more complex behavior was found in benzil for different quality crystals. These results have, of course, important implications for polymer and liquid crystal studies discussed below.

Simultaneous Brillouin-correlation light scattering results are presented for annealed and unannealed (as grown) crystals of benzil. Critical fluctuations are characterized for the LA a-axis mode governed by the elastic constant $c_{11}$

and are shown to contribute to this elastic anomaly in the high temperature phase. Both a central peak intensity anomaly and a critical relaxation time anomaly are characterized for unannealed crystals. These effects disappear in well annealed crystals. The critical relaxation behavior in benzil is coupled to the external stress compression wave generated by the mechanical refrigerator used to cool the sample. The latter interaction and relaxation anomaly are only observed with the stress applied along the b (or a) axis as required for a $c_{11}$ coupling. These observations are qualitatively analyzed employing the theory of anelastic solids with higher order fluctuation terms incorporated into the free energy expansion.

The a-axis polarized central peak observed in our previous Brillouin scattering experiments has been extensively studied by simultaneous measurement of Brillouin scattering and correlation spectroscopy. Our new findings are summarized as follows:

1. Correlation spectroscopy reveals a slow relaxation process in as grown samples in the polarized a-axis scattering.
2. The relaxation process is induced by external stress and depends on the direction of applied stress.
3. Relaxation time and counting rate (Rayleigh intensity) show critical anomalies around the transition temperature, as revealed by the previous Brillouin experiments.
4. No relaxation process or central peak could be observed in well annealed samples.
5. Brillouin frequency shifts and elastic constants are found to be independent of the thermal treatment of samples within the experimental uncertainty (~2%).

These results and their ensuing analysis suggest that annealable defects or impurities which are forced to move and relax in response to an external applied stress pulse are candidates for the origin of the central peak and relaxation process.

A complex elastic constant $c_{11}^*(\omega)$ is introduced through the theory of anelasticity and a dynamical susceptibility for the LA phonon propagating along the [100] direction is discussed. This susceptibility can be approximately decomposed into a Rayleigh component which shows intensity divergence and critical slowing down of the relaxation time and a component which shows a pair of LA phonon responses. These Rayleigh anomalies can be related to an anomaly in the elastic constant $c_{11}$. The $c_{11}$ anomaly arises from two separate contributions: a weak $c_{66}$ anomaly and a strong anharmonic coupling between the strain $(e_1+e_2)/2$ and fluctuations of the order parameter in the immediate vicinity of the transition.

Using the previous numerically fitted result for this elastic anomaly, these Rayleigh anomalies have been calculated. The calculation reveals somewhat weaker divergencies than are actually observed. Although the theory qualitatively explains the observed critical phenomena, higher order interactions between the order parameter and various strain should be taken into account. In addition, it is likely that the effects of the Brillouin zone boundary instability must also be considered.

Finally, it should be pointed out that these observations may be used as a sensitive indicator of crystal defect concentration, and whether or not these defects can be removed by any particular physical or chemical procedure. Perhaps more importantly, the dynamical properties of these defects can be ascertained with respect to both thermodynamic and fluctuation dominated critical behavior.

We are presently in the process of getting new data for lyotropic liquid crystals and polymers in melts, liquid crystals and solids. The polymer data are still beyond our current scope of interpretation but we are making progress on the liquid crystal systems.

The new data we have for dynamics and phase transition are on lyotropic liquid crystals. They are completely unique and novel and apparently give us better insight into liquid crystal dynamics than any other data I have

ever seen. The experiments deal with correlation Rayleigh light scattering, the results of which explore the low frequency dynamics of the model system sodium decyl sulfate/decanol/sodium sulfate/water. The data are actually more revealing than even we could have hoped. The enclosed figures show the data and represent our interpretation given below.

Figure 3 depicts the experimentally observed correlation time (in milliseconds) as a function of temperature for a particular sample (37:5:5:53 weight percent). These millisecond times correspond to kilohertz motional dynamics (slow) never seen before in such samples; they are apparently most revealing of the underlying kinetics. This dynamical behavior is essential for the physical properties of the system. Each peak or critical increase in the relaxation time as a function of temperature represents a "critical slowing down" or cooperative ordering interaction in the sample. These observations of critical behavior and new low frequency dynamics in a liquid crystal (polymer-like) sample have previously gone unnoticed. This is very well illustrated in fig. 3 by the superimposed summary of Brillouin data simultaneously obtained for the same sample. Only very slight (previously overlooked) changes take place in this latter form of light scattering. This is perhaps the clearest, most compelling argument for using all three energy regions of light scattering (i.e., Raman, Brillouin and Rayleigh) in studying dynamical behavior, phase transitions and critical phenomena in the condensed phase.

We believe we now have come up with a valid and physically important interpretation of these data. The overall general picture is presented in the next figures (fig. 4a,b,c). The important concepts concerning the above observations are: the 9°C anomaly in the relaxation time is the most intense and, therefore, should reflect the dynamics of a major fraction of the liquid; the 43°C anomaly is somewhat weak and extends over a wider temperature range and, therefore, should represent a more disordered but still abundent dynamical

fluctuation; and the last feature at 47°C is the broadest and weakest of the three anomalies and will be associated with even more diffuse behavior of minority components. It is important to note as one of the more significant and essential features of this data set that after each of the above three critical events the relaxation time returns to its normal background value of about 50μsec. This clearly and decisively illustrates the critical nature of these events. Moreover, it would seem apparent the 9°C feature deals with weak intermolecular interactions which the 47°C feature must arise from a more strongly interacting part of the system.

Figure 4a demonstrates ordering of disks which we believe are the major component of this micelle-like solution; it is these 1000 Å or larger disks which critically order and have their dynamics altered at 9°C. These disks are composed of sodium decyl sulfate and decanol with the polar ends of these molecules (represented by circles in figure 4b) on the outside and their polymer-like tails on the inside (figure 4c). The second relaxation time change at 43°C most likely arises from the polar head groups reorganizing on the surface of the micelles. This mechanism fits the experimental results in terms of intensity of the effect and strength of interactions. Head group rearrangement is certainly assisted by and mediated by the presence of ions and hydrogen bonded water at the micelle surface. The third relaxation time we have assigned to the hydrocarbon tail region and probably represents an "across the micelle" melting-like interaction. This motion would probably have the weakest light scattering interaction and relaxation time effect but would probably have the strongest intermolecular interaction potential. This latter point is at least partly due to probing considerations.

It is as yet too early to tell where these observations will lead us in terms of polymer dynamics. The fact that we have been able to obtain unique

and novel experimental results and interpret them in terms of a microscopic mechanistic model is encouraging for our polymer studies. As you will recall from our proposal, these model systems were a preliminary step towards the major undertaking in our effort. We now have the ability and experience to deal with more complex system.

## CUMULATIVE CHRONOLOGICAL LIST OF PUBLICATIONS


E.R. Bernstein and G.R. Meredith, Vibrational Spectra of Transition Metal Hexafluoride Crystals. I. Orthorhombic $MoF_6$, $WF_6$, and $UF_6$ Neat Crystals, Chem. Phys. 24, 289 (1977).

E.R. Bernstein and G.R. Meredith, Vibrational Spectra of Transition Metal Hexafluoride Crystals. II. Two-Particle and Mixed Crystal Spectra as Techniques for Determination of Densities of States, Chem. Phys. 24, 301 (1977).

E.R. Bernstein and G.R. Meredith, Vibrational Spectra of Transition Metal Hexafluoride Crystals. III. Exciton Band Structures of $MoF_6$, $WF_6$, and $UF_6$, Chem. Phys. 24, 311 (1977).

E.R. Bernstein and G.R. Meredith, Raman Spectra of $SiF_4$ and $GeF_4$ Crystals, J. Chem. Phys. 67, 4132 (1977).

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J.C. Raich and E.R. Bernstein, On the Phase Transition in Sym-Triazine - Mean Field Theory, J. Chem. Phys. 73, 1955 (1980).

J.C. Raich, E.R. Bernstein, and A. Yoshihara, Structural Transition and Elastic Anomalies in S-Triazine, $C_3N_3H_3$, Chem. Phys. Lett. 82, 138 (1981).

A. Yoshihara, W.D. Wilber, E.R. Bernstein, and J.C. Raich, On the Phase Transition in Benzil, J. Chem. Phys., submitted.

J.C. Raich, E.R. Bernstein, and A. Yoshihara, Theory of Structural Transformations in Orientationally Disordered Crystals, Trans. Am. Cryst. Assoc. 17, 1 (1981).

A. Yoshihara, J.C. Raich, and E.R. Bernstein, Light Scattering Study of the Phase Transition in Sym-Triazine, J. Cehm. Phys., submitted.

A. Yoshihara, J.C. Raich, and E.R. Bernstein, Critical Behavior in Annealed and Unannealed Benzil Crystals, J. Chem. Phys., submitted.

J.C. Raich and E.R. Bernstein, Comment on the Quasi-Harmonic Treatment of the Structural Phase Change in S-Triazine, J. Chem. Phys., submitted.

E.R. Bernstein, A. Yoshihara, and J.C. Raich, On the Phase Transition in Chloranil, to be submitted, J. Chem. Phys.

E.R. Bernstein, G-J. Wu, and A. Yoshihara, Phase Transitions in a Lyotropic Liquid Crystal, to be submitted, J. Chem. Phys.

## FIGURE CAPTIONS

### Figure 1

Polariton shifts in sym-triazine for the phonon at about $70cm^{-1}$ (90° scattering) with respect to different scattering angles. The mode is a rotatory mode of E symmetry. The small peak at ~ $75cm^{-1}$ in the 0° spectrum is associated with the system optics.

### Figure 2

Dispersion relation for polariton frequencies versus scattering angle for the phonon at $70cm^{-1}$ (90° scattering) in sym-triazine. The full circles and triangles show two different observed data sets taken on two independent samples. The vertical line at the triangle (ϯ) shows the average error in the observed data and the uncertainty in scattering angle is about ±0.3°.

### Figure 3

Rayleigh scattering (lower curve) and Brillouin scattering (upper curve) for the lyotropic liquid crystal SDS/decanol/sodium sulfate/$H_2O$. The peaks in the lower curve indicate phase transition and critical phenomena in the correlation function and relaxation times of the various dynamical degrees of freedom.

### Figure 4

(a) Mechanism believed to be associated with 9°C relaxation time anomaly.

(b) Representation of the polar head/water interface of the disk shaped structure in the liquid crystal. The 43°C anomaly is believed to be associated with the rearrangement of this interface and polar head region.

(c) A pictoral representation of the dynamics associated with the 47°C correlation function anomaly. The hydrocarbon tails represented by squiggly lines disorder or melt at T > 47°C.

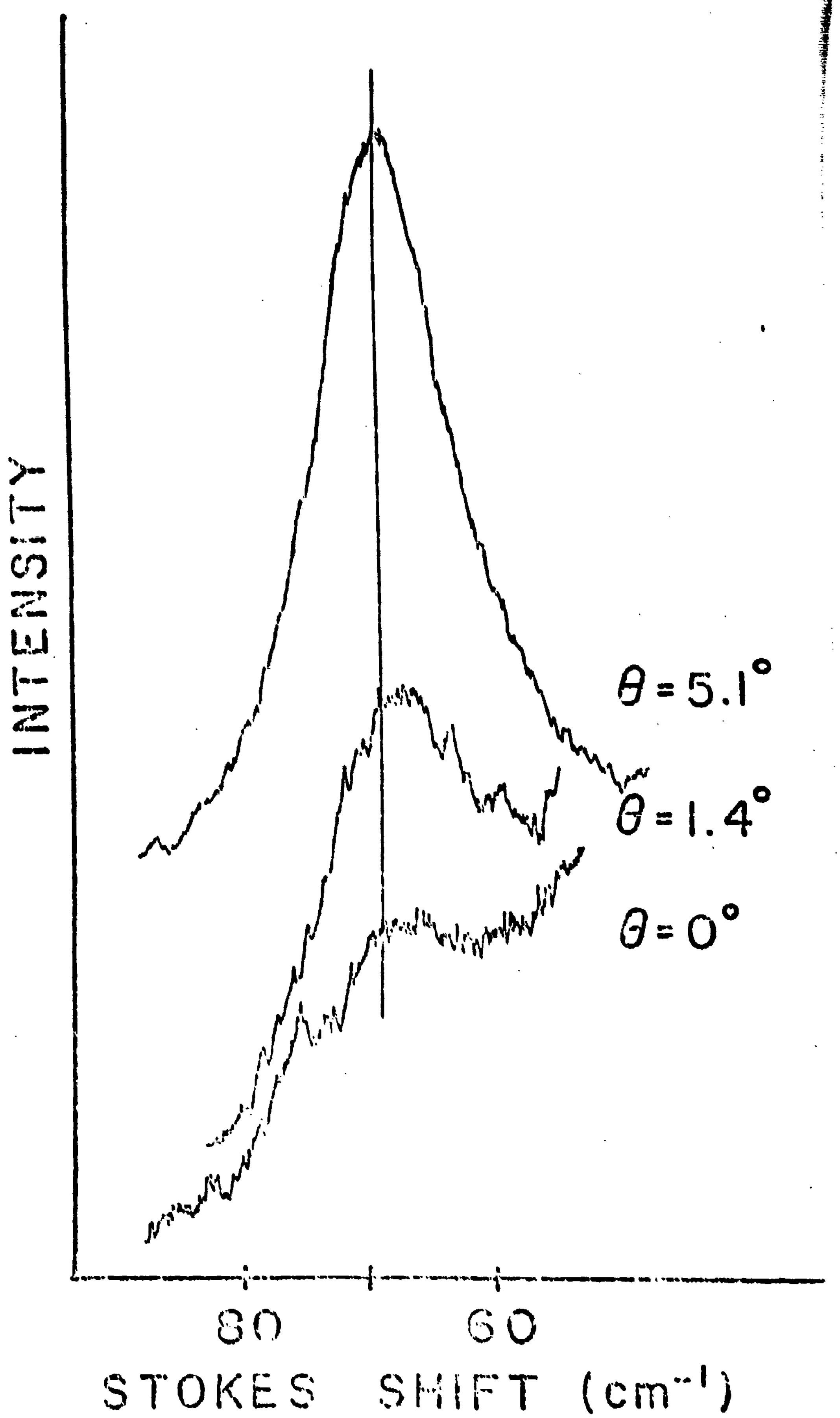


FIGURE 1

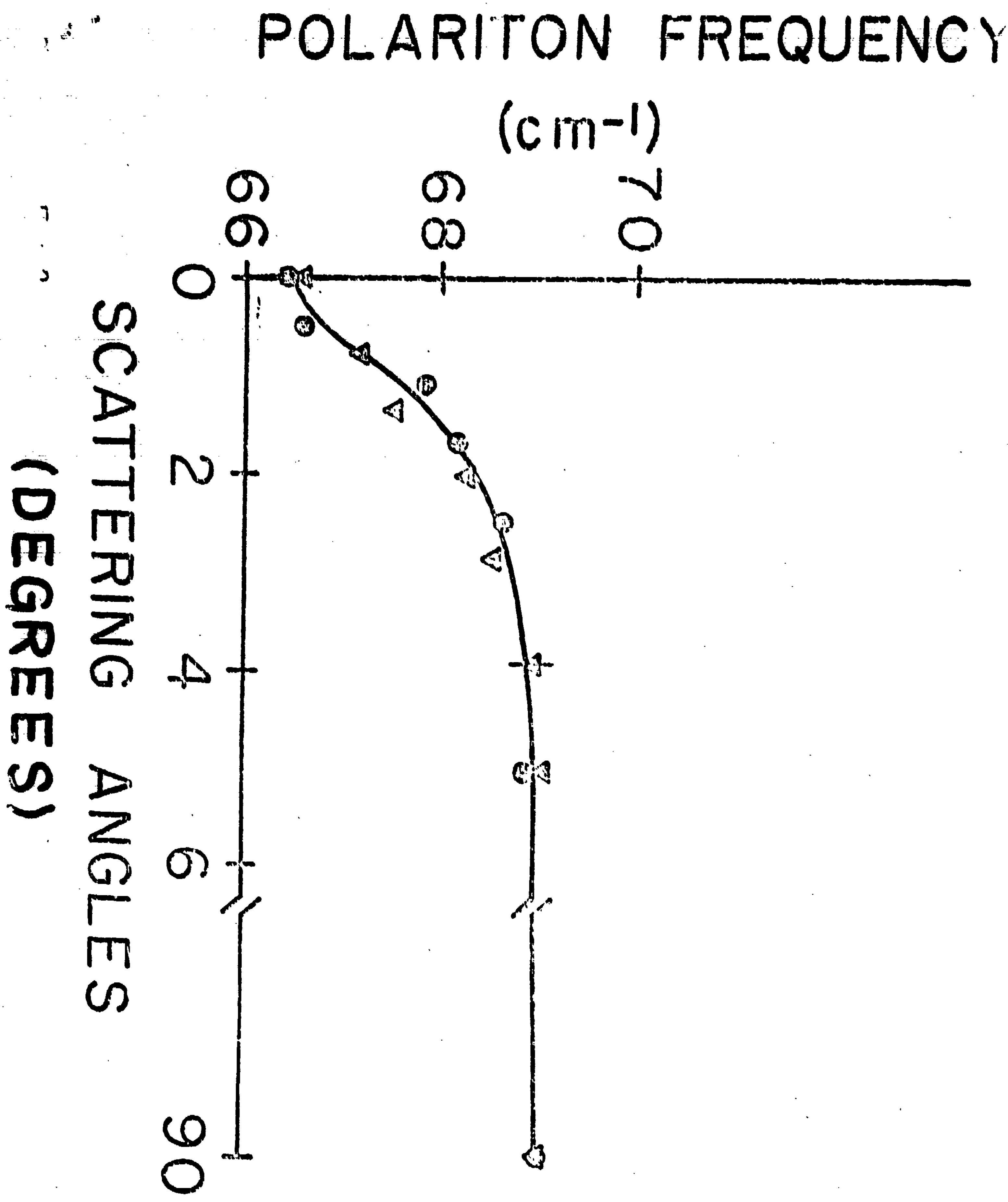
POLARITON FREQUENCY
(cm-1)
66
68
70
0
2
4
6
90
SCATTERING ANGLES
(DEGREES)

FIGURE 2

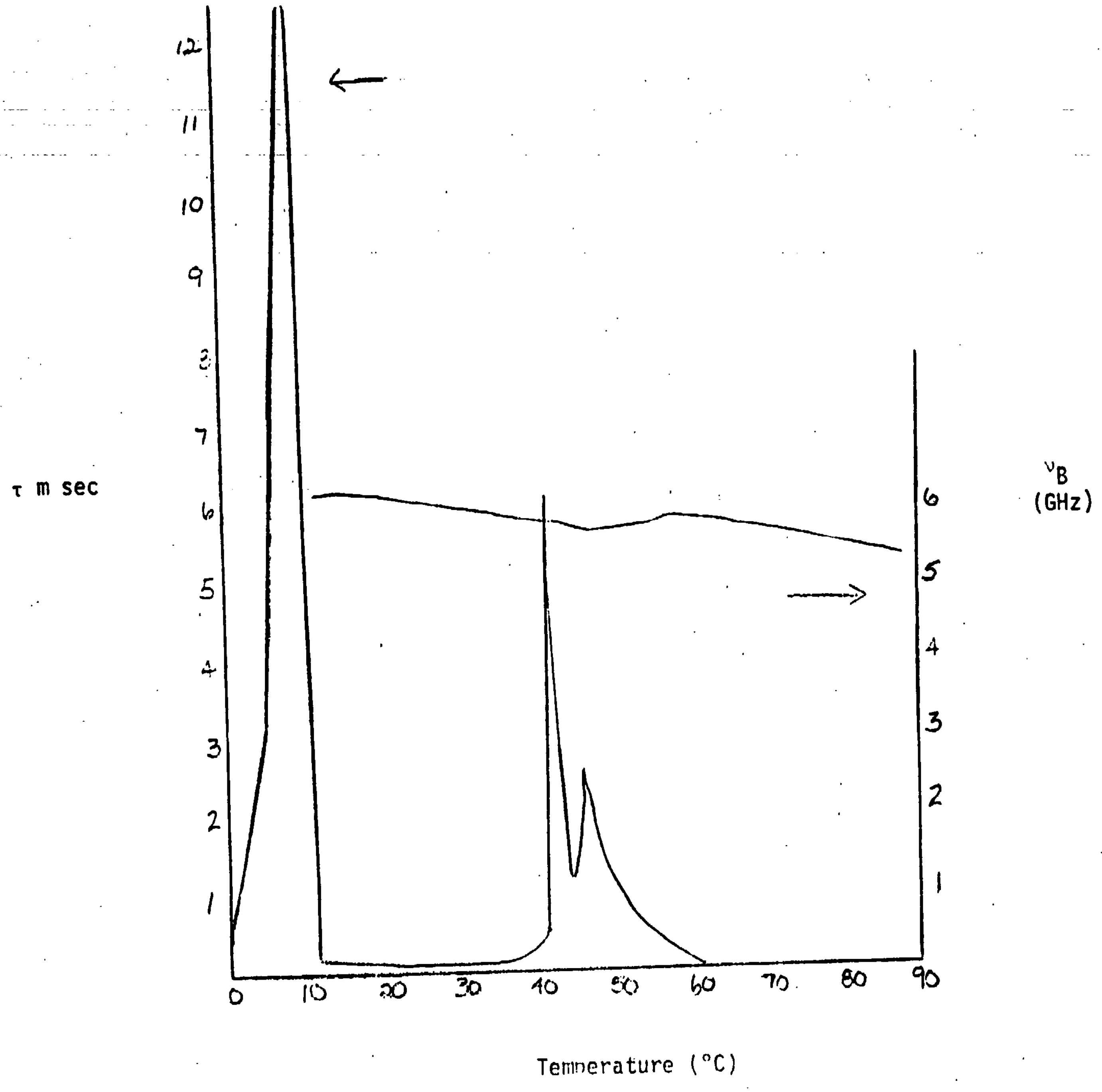


FIGURE 3

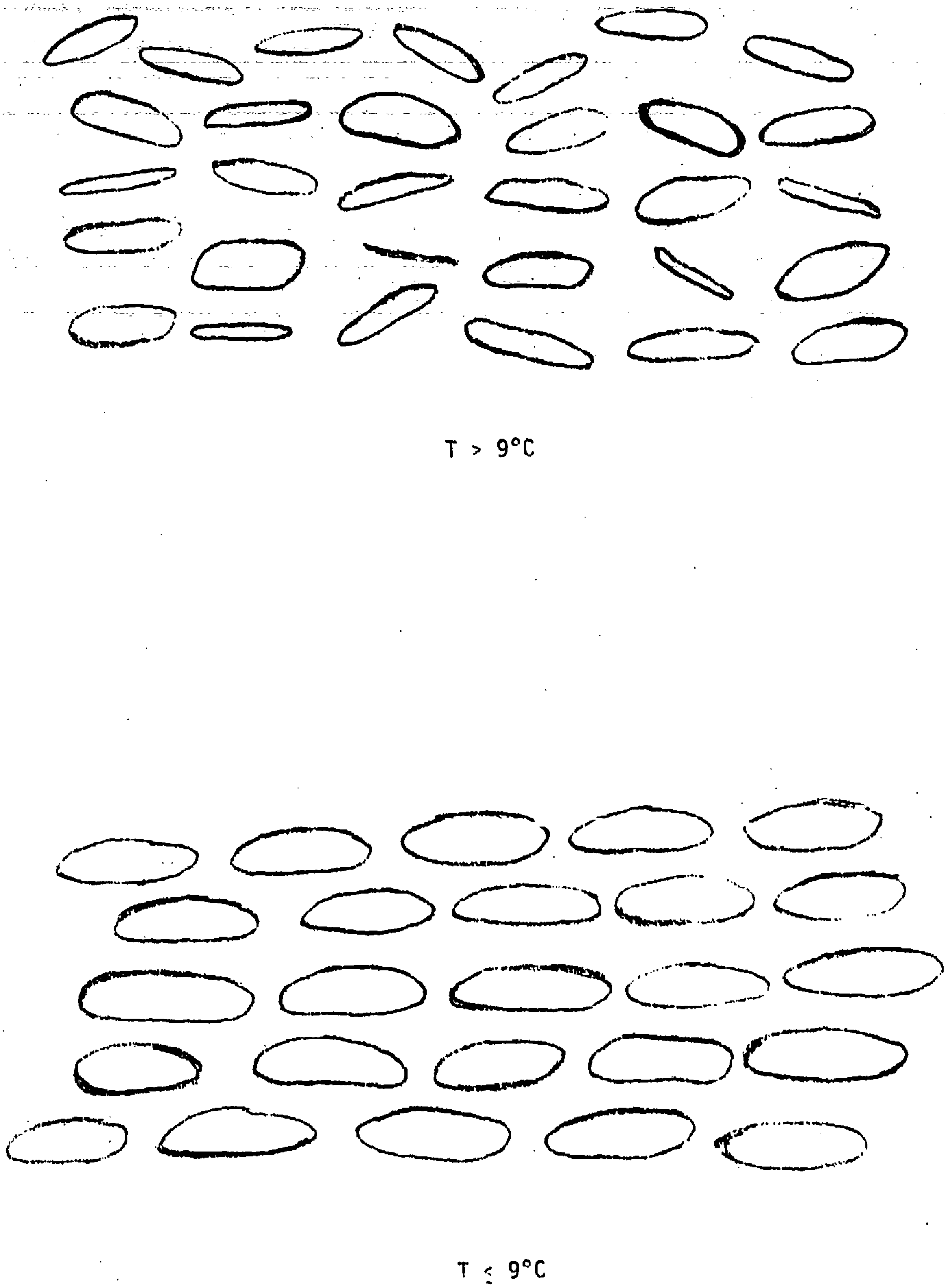


FIGURE 4a

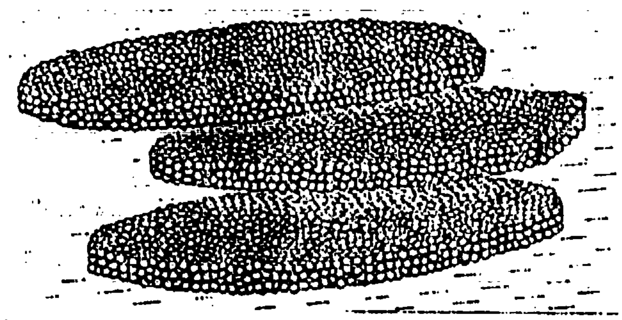

FIGURE 4b

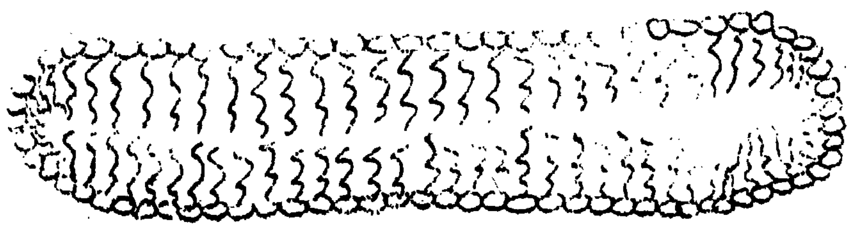

FIGURE 4c

## PROFESSIONAL PERSONNEL ASSOCIATED WITH THE RESEARCH EFFORT

| | | |
|---|---|---|
| Graduate Students: | T. Lewis | no degree |
| Postdoctoral Fellows: | B.B. Lal<br>K.M. Chen<br>A. Yoshihara<br>C-L. Pan<br>G-J. Wu | Ph.D's |
| Visiting Professor: | H. Yasuda | Ph.D. |

## INTERACTION

Seminars Given - Fall 1981

| | | |
|---|---|---|
| 1. | Michigan State University | November 4, 1981 |
| 2. | Wayne State University | November 5, 1981 |
| 3. | University of Michigan | November 6, 1981 |
| 4. | University of California - Los Angeles | November 30, 1981 |
| 5. | University of Southern California | December 1, 1981 |
| 6. | University of California - Riverside | December 2, 1981 |
| 7. | University of California - Irvine | December 3, 1981 |

Upcoming Seminars - Spring 1982

1. Xerox Corporation
2. State University of New York - Buffalo
3. Temple University - Philadelphia, Pennsylvania